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Radiochemical Investigation on Uranium Mill Tailings From Saskatchewan and Elliott Lake

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Abstract. A radiochemical investigation has been made of the Midwest Lake uranium tailings, as taken from a lysimeter at the Ontario Research Foundation, and Elliott Lake tailings, as taken from a lysimeter at CANMET. The distributions of Radium-226 and Thorium-230 show high concentrations in the fine, dense grains, and it appears that hematite may be the most prominent adsorbent mineral with sphalerite also playing a role. Leaching in dilute salt solutions shows that only a very small fraction of the Radium is removed by simple ion exchange, and suggests that the Radium and Thorium are nearly permanent in their binding to the tailings. The effect of arsenic in the tails is not seen to be a major influence. It seems likely that Radium is present in the hematite either as occluded ions or as trapped barium sulphate. Further radiochemical studies are recommended.

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EXECUTIVE SUMMARY

Samples of Midwest Lake and Elliott Lake uranium mine tailings taken from lysimeters were studied using radiochemical methods. The objective of this study was to determine the chemical and mineralogical location of the Radium and Thorium, so as better to understand the processes causing this adsorption, and to lead to methods of removing or otherwise controlling the potential for environmental pollution.

The results have shown that the majority of the radioactivity is concentrated on the finer grains, in agreement with frequent observations on other tailings. This phenomenon, seen also in tailings from other sources, has not yet been explained, and would likely be an important matter to investigate further.

The combined results of alpha-particle autoradiography and density separation have revealed that, as in the case of other tailings investigated, only certain of the grains are radioactive. On one sample, for instance, the grains which floated in $CHBr_3$ (density 2.87 grams per cc) accounted for about 98% of the mass of the sample but only about 2% of the Radium. Identification of the radioactive minerals led to the conclusion that the radioactive grains were of two types--some still containing undissolved uraninite and others containing adsorbed or occluded radionuclides. Hematite was most prominent among these latter minerals. Sphalerite was also seen to be radioactive. Clays were not detected in the samples studied, but likely may

have been washed away in the lysimeters.

Leaching studies were conducted in order to determine the nature and location of the binding of Radium and Thorium in the grains. The results were compared by computer analysis with the theoretical results predicted by a model based on our assumptions of several of the types of binding expected. This model is described here for the first time. It was found experimentally that only a very small fraction of the Radium is removed by simple ion exchange. Much of what is removed is seen to be buried in the matrix or to be entrapped in insoluble compounds. Barium sulphate is the most plausible trapping compound.

Leaching in dilute acid (0.1M HCl and 1.0M HCl) increased the amount of Radium leached somewhat, but made no great difference. The two acid strengths were not substantially different in effect.

A few experiments were done in a preliminary attempt to determine the binding of Radium as it is coprecipitated with ferric hydroxide and arsenate. In the presence of sulphate ions, the carrying of Radium was complete and rapid. This Radium was found to be only slightly removed under the conditions of the salt leaching experiments described above.

These experiments indicate the probable importance of further studies on the coprecipitation and leaching of sequestered Radium, with the expectation of leading to the further identification of sequestering minerals. This, in turn, could be of importance to the eventual concentration of the radioelements and to their ultimate containment.

INTRODUCTION

Objectives. The present study was undertaken to form an integral part of a larger study conducted under a tailings program of CANMET. Our role came as result of our experience with chemical studies of the leaching of Radium and Thorium, and our experience in attempting to identify the chemical and mineral locations of Radium and Thorium on tailings. The objectives were:

Selected specimens from core samples from the lysimeter at ORF and the 2 lysimeters in Ottawa will be provided by CANMET, as well as other designated samples, such as fresh tails from acid leaching. The research will consist of:

1) identification of ^{226}Ra and ^{230}Th in Midwest and Elliott Lake ores per size fraction of each designated specimen. The samples will consist of ore specimens, fresh tails and weathered tails (3 sample types from two locations = 6 sample types). Identification and location will be by:

a) autoradiography

b) alpha and gamma-ray spectroscopy

2) In consultation with Scientific Authorities, select fractions for at least 100 leach experiments under selected conditions (as H_2SO_4 to monitor the dissolution of ^{226}Ra and ^{230}Th.

3) Perform leaching studies on at least 100 samples from the 6 sample types, to determine the kinetics of dissolution of ^{226}Ra and ^{230}Th. The leech solutions will

be analysed for ^{226}Ra and ^{230}Th concentrations during and after leaching. CANMET will be provided with leach solutions for analyses other elements (Ni,Ca,Mo,Fe,S,As,U)

4) Examine grains during and after leach to determine changes in physical and chemical properties by:

-autoradiography, photomicrography

-SEM and microprobe (where appropriate),

Samples Received: The samples listed in Table I were received between early 1984 and early 1985. Some cores could not be studied because insufficient sample was received. Within this limitation, the samples listed in Table II were selected for more detailed study. This choice was made more or less arbitrarily, in an attempt to study all areas of the lysimeters (see Appendix I) assuming constant vertical composition. Each core was studied at its three levels, with the expectation (incorrect, as it now appears) that the liquid flow in the lysimeters was more or less vertical. Within each of these samples, several different size fractions (usually three) were studied, since the radioactivity distribution was expected to be different, based on earlier work. Following determination of the concentrations of Radium and Thorium in the respective samples, leaching experiments were done to determine the leaching kinetics and, through this, to determine the location of the radioelements within the grains.

Methodology. This section provides a brief discussion of the methods used. A detailed description of the methods will be found in Appendix II

TABLE I. Samples received in early 1984. All Samples were from the ORF lysimeter and are from Midwest Lake tailings.

January 25, 1984	A5246 + 47	(combined)	B-1.5		top
	48 + 49	"	" "		middle
	50 + 51	"	" "		bottom
	A5252 + 53	(combined)	B-8.5		top
	54 + 55	"	" "		middle
	56 + 57	"	" "		bottom
	A5270 + 71	(combined)	B-5		top
	72 + 73	"	" "		middle
	74 + 75	"	" "		bottom
	A5276 + 77	(combined)	E-5		top
	78 + 79	"	" "		middle
	80 + 81	"	" "		bottom
January 27, 1984	A5282 + 83	(combined)	J-7		top
	84 + 85	"	" "		middle
	86 + 87	"	" "		bottom
	A5264 + 65	(combined)	H-8.5		top
	66 + 67	"	" "		middle
	68 + 69	"	" "		bottom
	A5258 + 59	(combined)	H-1.5		top
	60 + 61	"	" "		middle
	62 + 63	"	" "		bottom
February 15, 1984	A5258 + 59(c)	12μ (comb.)	H-1.5	1+2	top
	60 + 61(c)	" "	" "	3+4	middle
	62 + 63(c)	" "	" "	5+6	bottom
	A5264 + 65(B)	12-74μ "	H-8.5	1+2	top
	66 + 67(B)	" "	" "	3+4	middle
	68 + 69(B)	" "	" "	5+6	bottom
	A5270 + 71(B)	12-74μ "	B-5	1+2	top
	72 + 73(B)	" "	" "	3+4	middle
	74 + 75(B)	" "	" "	5+6	bottom
	A5246 + 47(c)	-12μ "	B-1.5	1+2	top
	48 + 49(c)	" "	" "	3+4	middle
	50 + 51(c)	" "	" "	5+6	bottom
	A5252 + 53(c)	-12μ "	B-8.5	1+2	top
	54 + 55(c)	" "	" "	3+4	middle
	56 + 57(c)	" "	" "	5+6	bottom

TABLE I. (continued)

	A5258 + 59(B)	12-74μ	(comb.)	H-1.5	1+2	top
	60 + 61(B)	"	"	" "	3+4	middle
	62 + 63(B)	"	"	" "	5+6	bottom
	A5246 + 47(B)	12-74μ	"	B-1.5	1+2	top
	48 + 49(B)	"	"	" "	3+4	middle
	50 + 51(B)	"	"	" "	5+6	bottom
	A5252 + 53(B)	12-74μ	"	B-8.5	1+2	top
	54 + 55(B)	"	"	" "	3+4	middle
	56 + 57(B)	"	"	" "	5+6	bottom
February 29, 1984	A5264 + 65(c)	-12μ	"	H-8.5	1+2	top
	66 + 67(c)	"	"	" "	3+4	middle
	68 + 69(c)	"	"	" "	5+6	bottom
	A5270 + 71(c)	-12μ	"	B-5	1+2	top
	72 + 73(c)	"	"	" "	3+4	middle
	74 + 75(c)	"	"	" "	5+6	bottom
	A5276 + 77(c)	-12μ	"	E-5	1+2	top
	78 + 79(c)	"	"	" "	3+4	middle
	80 + 81(c)	"	"	" "	5+6	bottom
	A5282 + 83(c)	-12μ	"	J-5	1+2	top
	84 + 85(c)	"	"	" "	3+4	middle
	86 + 87(c)	"	"	" "	5+6	bottom
	A5276 + 77(B)	12-74μ	"	E-5	1+2	top
	78 + 79(B)	"	"	" "	3+4	middle
	80 + 81(B)	"	"	" "	5+6	bottom
	A5282 + 83(B)	12-74μ	"	J-5	1+2	top
	84 + 85(B)	"	"	" "	3+4	middle
	86 + 87(B)	"	"	" "	5+6	bottom

February 1985 — 12 tailings samples from the Elliott Lake region:

Lysimeter A : top section, 2nd from top, 3rd, 4th and 5th from top, bottom section.

Lysimeter B : top section, 2nd, 3rd, 4th and 5th from top and bottom section.

TABLE II. Samples studied by leaching in 0.1 M KCl. Each sample was tested at 6 times for each of ^{226}Ra and ^{230}Th.

a) Midwest Lake Tailings - ORF Lysimeter

H	1.5	< 12μ	top
H	1.5	< 12μ	middle
H	1.5	< 12μ	bottom
H	1.5	combined	top
H	1.5	"	middle
H	1.5	"	bottom
H	1.5	12 - 74μ	top
H	1.5	12 - 74μ	middle
H	1.5	12 - 74μ	bottom
B	5	< 12μ	top
B	5	< 12μ	middle
B	5	< 12μ	bottom
B	5	combined	top
B	5	"	middle
B	5	"	bottom
B	5	12 - 74μ	top
B	5	12 - 74μ	middle
B	5	12 - 74μ	bottom
J	5	combined	top
J	5	"	middle
J	5	"	bottom
J	5	12 - 74μ	top
J	5	12 - 74μ	middle
J	5	12 - 74μ	bottom
J	5	< 12μ	top
J	5	< 12μ	middle
J	5	< 12μ	bottom
B	1.5	combined	top
B	1.5	"	middle
B	1.5	"	bottom

b) Elliott Lake tailings.

Lysimeter A : top, 2nd, 3rd, 4th, 5th from top and bottom section.

Lysimeter B : top, 2nd, 3rd, 4th, 5th from top and bottom section.

In essence, our methods are all radiochemical. The analytical methods involve standard radiochemical analysis by one of the following methods:

i) Chemical processing of the sample (including dissolution of solids, when necessary) followed by chemical isolation of the radioelement in question. Measurement of the radioactivity in these cases was done by α-particle spectroscopy and was usually unambiguous as to both the identity and the intensity of the alpha emissions.

ii) Physical handling of the sample so as to make its geometrical form and location accurately reproducible. Measurement of the radioactivity was done by high-resolution γ-ray spectroscopy. This method is particularly convenient for Radium-226, but it is not as reliable on samples which have undergone chemical action.

iii) In some cases, measurement of the radioactivity was done using low-resolution γ-ray spectroscopy. This simple method was used only in cases where no ambiguity could result from the loss of resolution and when the higher sensitivity would be advantageous.

Methods to locate the radioelements more precisely have two distinct objectives: i) to identify those grains which are radioactive, with a view to identifying the mineral concerned. A more refined aspect of this is to isolate grains which are radioactive only in spots[1,2] and to distinguish chemically or mineralogically the different surfaces which lead to this selective distribution. ii) to determine the chemical bonding holding the radioelements and their depth in the grain. This is

TABLE III. Results of radiochemical analysis of the tailings samples. All values are the average of two determinations. (T, M and B are Top, Middle and Bottom)

Samples		^{226}Ra pCi g^{-1}	^{230}Th pCi g^{-1}	Residue pCi g^{1}
B5 12-74μ	T	2819	1626	667.4
	M	1977	696	476
	B	2319	1977	947
B5 <12μ	T	11704	9387	2469
	M	12455	16472	2340
	B	12278	13238	925
B5 combined	T	551	471	111
	M	711	249	58
	B	1099	1589	159
H 1.5 combined	T	1555	929	983
	M	1689	605	94
	B	786	443	112
H 1.5 12-74μ	T	2985	1308	146
	M	3563	745	167
	B	3002	1715	209
H 1.5 <12μ	T	3736	17445	23920
	M	15267	17183	608
	B	10861	14567	1306
J 5 combined	T	772	1795	1938
	M	112	22	2
	B	28	11	4
J 5 12 - 74μ	T	3198	1055	994
	M	-	-	-
	B	-	-	-
J 5 <12	T	13539	16568	1560
	M	10380	15887	4964
	B	-	-	-
B 1.5 combined	T	727	821	80
	M	871	241	50
	B	516	569	90

done by time-dependent leaching studies[2-5] in gentle reagents. The principles of this method will be discussed further below.

RESULTS.

Radioactivity distribution. The concentrations of Radium-226 and of Thorium-230 were determined by the standard methods used in our laboratory (see Appendix II) following opening up of the mineral by treatment with boiling HF-$HClO_4$. The results of this analysis are given in Table III. In all cases, a small portion of the sample was found to be insoluble. The radioactivity of this insoluble material is also shown as Column 4 in Table III. Studies of a few samples of this insoluble material gave the results shown in Table IV.

Table IV. X-ray identification of some undissolved Midwest Lake grains

Sample	Minerals found
H 1.5 comb top	zircon,graphite,anatase
H 1.5 comb mid	zircon,graphite,tourmaline, anatase,rutile,corundum
H 1.5 comb bot	zircon,graphite,anatase, tourmaline,rutile

From the results given in Table III, it can be seen that the distribution of both ^{226}Ra and ^{230}Th shows markedly higher concentration in the smaller grains. This follows the pattern observed in a variety of other cases[4,6]. No satisfactory explanation has been given except the suggestion that the smaller grains have a larger surface area. It seems likely from the

present work that some chemical mechanism might be involved, although nothing specific is evident at present.

Density separation. The separation of grains on the basis of their density was done through the usual method of differential sedimentation in dense liquids. The liquids used were Bromoform ($CHBr_3$) and Diiodomethane (CH_2I_2), whose densities are 2.87 and 3.33 g/cc, respectively. The sample studied in this manner was B 1.5, bottom, combined, whose bulk radioactivity showed 503 pCi of Radium-226 per gram. The results of the separation are shown in Table V.

Table V. Results of density separations. Note that the $CHBr_3$ heavy fraction was further separated using CH_2I_2

		Mass		Radioactivity	
		grams	%	pCi/g	%
$CHBr_3$	Light	1.060	98.0	128	2.1
	Heavy	0.021	2.0	4321	97.9
CH_2I_2	Light	0.006	0.6	777	12.6
	Heavy	0.015	1.4	5243	85.3

It is very clear from the data in Table V that the Radium is located primarily on the denser grains. A similar observation was made earlier[1] regarding tailings from the Beaverlodge area. At that time, it was noticed that the radioactive fractions were not only very dense, but also dark in colour. Preliminary observation of the present samples support this. Although the above activity values are perhaps only approximate, in that they may not be accurately representative of the larger bulk of tailings, the results clearly demonstrate the trend of increasing activity

with increasing particle density. Optical examination of the fractions indicated that the separation was imperfect, especially for mixed grains. It should be noted that the separation achievable by this method is complete only for discrete grains of single minerals. Mixed grains may well place some minerals in the wrong fraction. Thus, the true radioactivity distribution may be even more strongly toward denser particles. It was also noted, furthermore, that these same fractions segregated the dark-coloured grains from the light-coloured ones. This concurs with similar observations made on Beaverlodge tailings. Visual examination did not reveal the presence of clays in the sample. Thus, the well-known ability of clays to take up foreign ions by ion exchange cannot explain the results of these measurements.

Autoradiography. Autoradiographic measurements were made on representative grains from the different density fractions, to determine whether the radioactivity was widely distributed or concentrated on certain select mineral grains. The grains were visually separated into several groups, which were subsequently identified by x-ray powder diffraction. Included also were some grains known or suspected to be non-radioactive, in order to get a more comprehensive picture of the radioactivity distribution. The results of this investigation are given below in Table VI.

Table VI. Some mineralogical observations on autoradiographed grains.

Grain description	Radioactivity	Mineral
black, resinous, some crumbly	very strong	uraninite
greenish, black inclusions	strong	pyrite,uraninite
hard, dark red, some with crumbly exterior	less strong	hematite
light green, translucent	medium	sphalerite
light brown, translucent	medium	sphalerite
light pink, translucent	weak	zircon
clear, colourless, vitreous	very weak	quartz
clear, dark red, adamantine	inactive	rutile
black, metallic to vitreous	inactive	magnetite
whitish to light greenish	inactive	annabergite

Other, non-radioactive minerals were present, some of which could be identified visually. These include pyrrhotite, galena and probably hornblende.

Thus far, it appears that hematite seems to be the most prominent radioactive tailings mineral (other than uraninite, whose presence most likely results from incomplete initial leaching). It is not as yet certain why this is so, although some interesting experiments to be described below may shed some important light on this question. It seems possible that some of the 'crumbly' surface may have been precipitated onto the previously existing surface during the lime neutralization. The action of sphalerite has not been explained. The formation of ferric arsenate is conceivable, and may also have contributed to the adsorption of Radium on hematite. Preliminary experiments seem to show that arsenic is of lesser importance.

Theory of leaching studies. A large fraction of our program revolves around studies of the rate of leaching of Radium and

Thorium from the tailings. The rationale for this type of study has never been published in detail[2,3,5], so it seems useful to describe it at this point. Basically, it involves the recognition that ions (such as Ra^{++}) may be held in the solid in several ways:

1. as exchangeable ions on the surface
2. as exchangeable ions in a diffusion barrier on the surface
3. as part of a matrix which dissolves slowly
4. as part of a matrix which does not dissolve
5. others.

Only the first three of these need be considered.

The first of these is believed to be quite common and comprises a good portion of clay chemistry and the chemistry of many soils. The reaction involves the displacement of one ion on a surface by another:

$$M_1^{++} + M_2Soil \rightleftharpoons M_2^{++} + M_1Soil \qquad [1]$$

Given the proper chemical circumstances, this reaction will proceed toward an equilibrium at a rate described by a first order equation:

$$[M_2^{++}] = b\,(1 - e^{-rt}) \qquad [2]$$

where [ ] represents the concentration in solution, b is a constant related to the total quantity of exchangeable ion available for reaction per litre of solution, r is a rate constant equal to 0.693/c, where c is the half-time for the exchange, and t is the time. In the present case, we have

$$2K^+ + Ra^{Surface} \rightleftharpoons Ra^{++} + K_2^{Surface} \qquad [3]$$

and [2] becomes

$$[Ra^{++}] = [Ra]_R (1 - 2^{-t/c}) \quad [4]$$

where $[Ra]_R$ signifies total replaceable Radium per litre of solution. The reaction rate, and consequently the half time, will depend on the concentration of the replacing ion (in our case K^+), the temperature, the reactivity of the surface and other parameters.

The second process for leaching trace elements from mineral grains is essentially the same as the first, but differs in that the exchange sites are not at the surface. Thus, the rate determining step in the leaching is not the exchange but rather the diffusion of the ion from the exchange site out to the surface (or of the replacing ion inward). As the process goes on, the diffusion distance increases, leading to a parabolic dependence on the time:

$$\text{Rate} = DA[Ra]_R W/\delta V = d[Ra^{++}]/dt \quad [5]$$

where A is the area, D is the diffusion coefficient, W is the weight of the solid, V is the volume of the solution and δ is the diffusion distance. From this,

$$[Ra^{++}] = a\, t^{1/2} \quad [6]$$

where a is as function of the total exchangeable radium in the diffusion barrier, and other parameters:

$$a = A\,[Ra]_R.2DW/V. \quad [7]$$

The third class of reactions[2] is that of the insoluble compound which must dissolve slowly in order to release entrapped Radium ions. Such a case would be that in which Radium is held in a matrix of an insoluble Barium salt--$(Ba,Ra)SO_4$ is the most obvious example. This sort of reaction has been observed

prominently in the leaching of mixed soil samples from Port Hope, Ontario, where $BaSO_4$ was identified by x-ray diffraction. The dissolution in this case is likely to proceed with a linear dependence on time, modified only by a rather slow dependence on the decreasing surface area:

$$[Ra^{++}] = f\ t \qquad [8]$$

The full equation then becomes

$$[Ra] = a\ t^{1/2} + b\ (1 - 2^{-t/c}) + f\ t. \qquad [9]$$

Salt leaching. We have subjected 27 samples of Midwest Lake tailings to 6 tests each to determine the leachability of ^{226}Ra and ^{230}Th in 0.1M KCl. Twelve samples from Elliott Lake were similarly studied. The overall results were found to show quite uniformly that only a small fraction of the radioactivity was leached within the space of three hours. This contrasted markedly with the results of similar studies on Beaverlodge tailings, in which up to 60-70% of the Radium was removed within the first 30 minutes or so by a similar treatment.

This result could come from either of two causes: i) the Radium could be deeply buried within the grain and thus not be susceptible to surface exchange; ii) the Radium could be trapped in an insoluble compound, such as $Ba(Ra)SO_4$ or perhaps $(Ba(Ra))_3(AsO_4)_2$ such that the exchange equilibrium (Equation [3] is shifted very far to the left. Considering the dynamics of ore leaching processes, the latter seems to be more likely. This could be checked by leaching the tailings in a medium which would dissolve $BaSO_4$ or $Ba_3(AsO_4)_2$, such as DTPA or EDTA[2].

The Radium which was leached off in the present experiments

was analysed in terms of the simpler formula

$$[Ra^{++}] = a\ t^{1/2} + b\ (1 - 2^{-t/c}) \qquad [10]$$

with the intention of decreasing the number of variables available, and with the recognition that in some instances the need for the full Equation [9] would be made evident by a linear deviation of the model calculations from the experimental data. The results of this attempted data fitting are shown in Table VII.

It is seen that the results can be put into four groups:

i) those for which Equation 10 applies, indicating that both types of exchange reaction occur

ii) those for which only the surface exchange appears, and Equation [4] is valid

iii) those for which only the diffusion-controlled exchange occurs, and Equation [6] is valid, and

iv) those for which a noticeable linear component is present, and the reaction would better be analysed through Equation [8] or perhaps Equation [9].

No regularity of these samples is evident from the grouping in Table VII. This may be due in part to the way in which the lysimeters were constructed.

Acid leaching. Several samples were subjected to leaching in 0.1M HCl and in 1.0M HCl. The simple test leach was run for 180 minutes. The results showed that considerably more Radium was removed from the tailings, but still only a fraction of the total. There was only very little difference between the weaker

Table VII. Values of the parameters a,b and c for Equation [10] giving the best visual fit to the leaching data.

a) Midwest Lake Tailings

Lab No.	Sample	description		a	b	c	Group
1	B5	top	comb	10	10	0	ii
2	B5	mid	comb	0	--	2	iii
3	B5	bot	comb	8	20	1	i
4	B1.5	top	comb	28	15	0	ii
5	B1.5	mid	comb		linear		iv
6	B1.5	bot	comb		linear		
7	H1.5	top	comb	13	2	3	i
8	H1.5	mid	comb	8	5	2.6	i
9	H1.5	bot	comb	0	-	1.7	iii
10	B5	top	12-74μ	31	3	3.5	i
11	B5	mid	12-74μ	13	3	1.3	i
12	B5	bot	12-74μ	15	1	2	linear
13	B5	top	-12μ	53	2	2	i
14	B5	mid	-12μ	48	2	1	i
15	B5	bot	-12μ	37	1	0	ii
16	H1.5	top	12-74μ	8	2	4	i
17	H1.5	mid	12-74μ	5	1	4	linear
18	H1.5	bot	12-74μ	5	2	2.3	i
19	H1.5	top	-12μ	63	1	0	ii
20	H1.5	mid	-12μ	73	2	1.6	i
21	H1.5	bot	-12μ	21	2	1.3	i
22	J5	top	comb	15	20	0	ii
23	J5	mid	comb	too low to analyse			
24	J5	bot	comb	too low to analyse			
25	J5	top	12-74μ	24	2	2.2	i
28	J5	top	-12μ	5	1	1	ii
29	J5	mid	-12μ	22	1	2.2	i

b) Elliott Lake Tailings

	Sample	a	b	c	Group
A	top	1.4	1.0	0.006	i
A	2nd	1.8	1	0	ii
A	3rd	2.4	1	0	ii
A	4th	4.5	1	0	ii
A	5th	6.0	3	0	ii
A	bot	15	1	0	ii
C	top	too low to analyse			
C	2nd	too low to analyse			
C	3rd	2.9	2	0	ii
C	4th	3.5	2	0	ii
C	5th	2.7	1	0.11	i
C	bot	4.8	1	0.35	i

Table VIII

Acid Leaching

The very fine tailings from samples H-1.5, B-5 and J-5 were leached with 0.1 M HCl.

Sample	Time	^{226}Ra, pc	^{230}Th, pc	Solvent
H-1.5 A5258 + 59 (c) -12μ	3 hrs.	831.3 + 26 22.3%	1228.9 + 31 7.0 %	0.1M HCl
H-1.5 A5260 + 61 (c) -12μ	3 hrs.	927.8 + 23 6.1%	1147.3 + 25 6.7%	0.1M HCl
H-1.5 A5262 + 63 (c) -12μ	3 hrs.	777.4 + 23 7.2%	1256.6 + 26 8.6%	0.1M HCl
H-1.5 A5258 + 59 (c) -12μ	3 hrs.	978.2 + 25 26.2%	1442.0 + 33 8.3%	1 M HCl
H-1.5 A5260 + 61 (c) -12μ	3 hrs.	1151.8 + 36 7.5%	1781.1 + 30 10.4%	1 M HCl
H-1.5 A5262 + 63 (c) -12μ	3 hrs.	928.9 + 36 8.6%	1511.9 + 26 10.4%	1 M HCl
B-5 A5270 + 71 (c) -12μ	3 hrs.	838.9 + 23 7.2%	413.7 + 15 4.4%	0.1M HCl
B-5 A5272 + 73 (c) -12μ	3 hrs.	747.4 + 21 6.0%	1050.3 + 23 6.4%	0.1M HCl
B-5 A5274 + 75 (c) -12μ	3 hrs.	941.3 + 25 7.7%	807.5 + 21 6.1%	0.1M HCl
J-5 A5282 + 83 (c) -12μ	3 hrs.	866.0 + 23 6.4%	1040.3 + 24 6.3%	0.1M HCl
J-5 A5284 + 85 (c) -12μ	3 hrs.	522.2 + 17 5.0%	1074.2 + 24 6.8%	0.1M HCl
J-5 A5286 + 87 (c) -12μ	3 hrs.	18.7 pc+1.0	13.2 + 0.8	0.1M HCl

H-1.5 A5260 + 61 -12μ	3 hrs. + 32.24 mg Fe wire	847.5 + 22 5.6%	1068.8 + 24 6.2%	0.1M HCl
H-1.5 A5260 + 61 -12μ	4.8 days	1003.3 + 23 6.6%	1086.1 + 25 6.3%	0.1M HCl
H-1.5 A5260 + 61 -12μ	4.8 days + 33.65 mg Fe wire	1047.7 + 24 6.9%	1123.4 + 25 6.9%	0.1M HCl

and the stronger acid experiments. The data for 0.1M and 1.0M Hydrochloric acid are given in Table VIII.

Reduction leaching. One of the concerns to be addressed in the study of these tailings was the role of Arsenic, which is prominent in some of the minerals. It was noted that the initial leaching which produced the tailings was an oxidising leach. It is possible that during this step arsenic could become fully oxidised and thus trap Radium as the insoluble $(Ba,Ra)_3(AsO_4)_2$. It was felt that a useful experiment would be to conduct a leach test under reducing conditions in order to reduce arsenate to arsenite. The reducing agent selected was metallic iron, which was added to the acidic solution as pure iron wire. The reactions and standard electrode potentials are:

$$Fe^{++} + 2e^- = Fe \qquad -0.440 \text{ volts}$$

$$H_3AsO_4 + 2H^+ + 2e^- = HAsO_2 + 2H_2O \qquad +0.559 \text{ volts}$$

$$H_3AsO_4 + 2H^+ + Fe = HAsO_2 + Fe^{++} + 2H_2O \qquad +0.119 \text{ volts}$$

This shows that the reaction should proceed as indicated.

The results of two such experiments (see Table VIII) fail to show any effect of the reduction. It must be emphasized that this is not a definitive result, since the reduction may still be kinetically very slow, or the desired reaction may be stoichiometrically overwhelmed by other extraneous reductions. This type of experiment should be repeated using other reducing agents.

Ferric hydroxide carrying. Tests were done to check on the plausibility of Radium being carried irreversibly with iron hydroxide. The results would in no case prove that this had been the means of trapping the radionuclides, but could show whether

or not this mechanism would be worth considering as a possible explanation. Two 50-ml solutions were made up to contain about 20 mg Fe^{+++} and 250 pCi Ra^{++}. To one of these was added 50 mg Sodium Arsenate. Both solutions were treated with Sodium Hydroxide to reach a pH of 8. The suspension was allowed to settle for 15 minutes and then was centrifuged. The supernatant solution was decanted through a 0.45μ filter. No Radium was detectable in the filtrate.

The ferric hydroxide precipitates were leached with 100 ml of 0.1M KCl solution. The results of these leach experiments showed no Radium removed from the precipitate in presence of Arsenate, and only 3.2% removed from the precipitate without arsenate. Once again it is likely that the highly adsorbent Ferric hydroxide holds the Radium so tightly that the equilibrium[3] is shifted far to the left. This could be better tested by leaching using a higher-charged cation such as Ca^{++} although the pertinence to the present study would be diminished by the low solubility of $CaSO_4$. The effect of arsenic is notable and shows that the presence of AsO_4^{-3} in the leach liquors could explain the apparent resistance of Radium to this type of leaching. The present work does not provide adequate proof, however.

These results show i) that ferric hydroxide is a good carrier for Radium if the pH is high, ii) little or no Radium is removed by ion exchange in 0.1M KCl and iii) the presence of arsenate in the precipitation solution has very little effect, but may serve to hold the Radium somewhat more tightly against ion exchange.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions. The experimental work described in the present report has led to a number of interesting conclusions. To some extent, we must caution against over-generalization from this work, inasmuch as the experiments were performed on a small number of samples whose chemical history was not accurately known. Nevertheless, it appears that some potentially important results have emerged. These have all been discussed in the Report above, and will be enumerated here. Note that points 1 to 6 apply only to the Midwest Lake tailings. The reason for this is that the Elliott Lake tailings as received were too finely ground to be studied under an ordering optical microscope.

1. The finer grains are more radioactive than the coarser ones.

2. Only some grains are radioactive. These radioactive grains appear to be characterized by higher density (greater than 3.33 grams per cc) and by darker colour.

3. Some of the radioactive grains contain unleached uranitite.

4. On one sample, which may be typical, 98% of the radioactivity was contained in about 2% of the mass.

5. The most active grains (other than uranitite) were hematite. Somewhat less active were grains of sphalerite.

6. Grains of zircon and quartz were weakly active, while rutile, magnetite and annabergite seem to be inactive.

7. Only a small fraction of the Radium and Thorium could be leached by simple ion exchanging reagents (0.1M KCl).

8. Dilute acid (0.1M and 1.0M HCl) was able to remove less than 10% of the Radium in 3 hours.

9. The leaching kinetics were analysed according to a model which is described in detail in this report.

10. This analysis shows the presence of Radium in three different types of binding: directly exchangeable, exchangeable in a diffusion barrier and slowly dissolvable.

11. Preliminary experiments showed Radium to be quantitatively precipitated along with ferric hydroxide at pH 8, with or without arsenate being present.

12. Preliminary experiments showed that Radium carried down in this way with ferric hydroxide leaches only very slightly by ion exchange.

13. Attempts to identify an effect caused by the presence of arsenic were not successful.

Recommendations. The following recommendations refer to the continued attempt to gain a better understanding of the chemical and physical behaviour of Radium and Thorium in uranium mine tailings:

1. Insofar as it may be possible, further laboratory studies should be conducted using tailings of accurately known composition and chemical history.

2. Specific tests should be continued to investigate the possible applicability of the reaction model to specific fractions of the tailings.

3. Larger quantities of separated minerals should be

studied by autoradiography and by kinetic leaching to determine the generality of the results of the present study.

4. In particular, studies should be extended on the hematite and sphalerite fractions, to be sure that the present results are truly representative of the larger body of Midwest Lake tailings.

5. Parallel studies should be undertaken to ascertain the detailed nature of the carrying of Radium by ferric hydroxide using CO_3^{--} SO_4^{--} AsO_4^{-3} ions in the solutions.

6. These studies should be correlated with available information on the transformation of ferric hydroxide into hematite.

7. The possible role of jarosite in carrying Radium should be investigated further[7].

8. On a larger scale, the possible separation of the more highly radioactive minerals should be attempted, in an effort to reduce the volume of the tailings and make their handling more feasible.

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5. D. R. Wiles. Water Air and Soil Pollution 20, 99 (1983).

6. J. D. Shearer and G. F. Lee. Health Physics, 1, 217 (1964).

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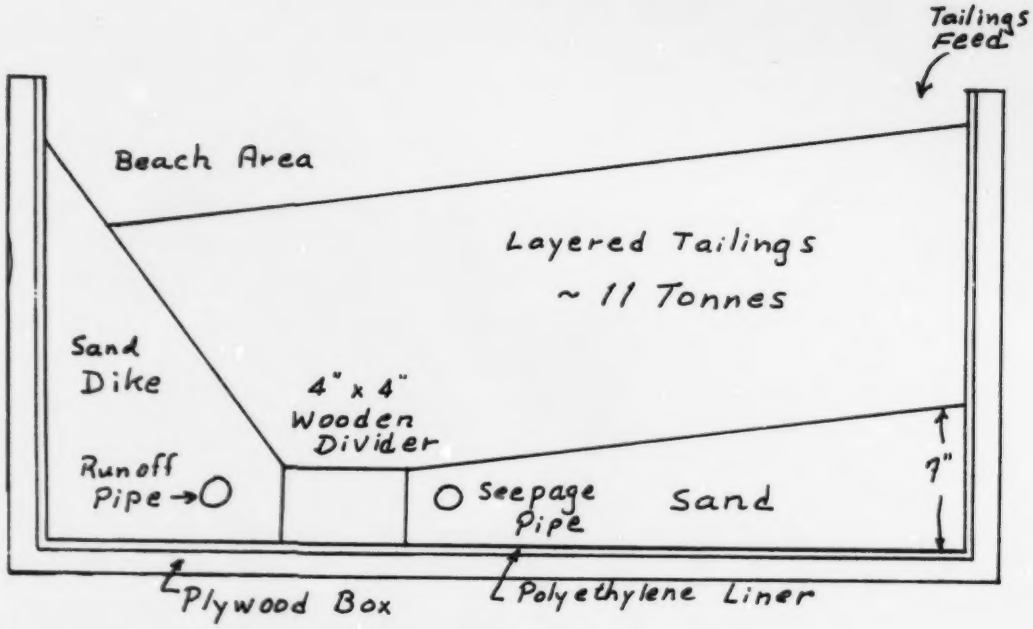
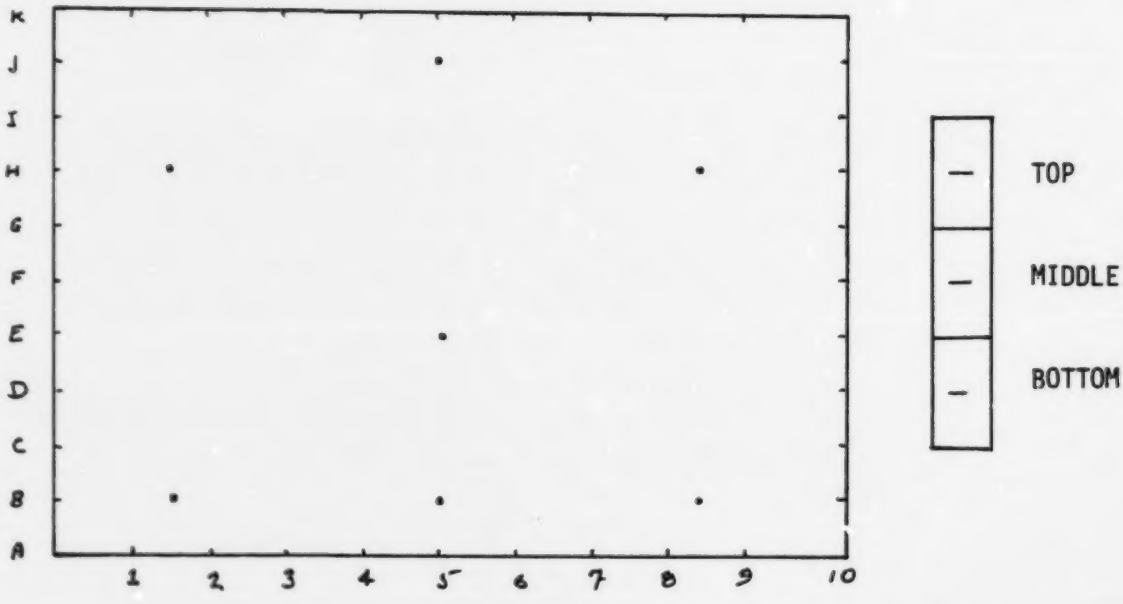
APPENDIX I: ORF Lysimeter



SIDE ELEVATION



Plan. Cores were taken at the points indicated

Appendix II

Experimental Procedures

Sample Digestion.

Small amounts of the samples (0.1-0.5 g) were digested using conc. HNO_3 to oxidize any organic material, followed by digestion with 48% HF. The HF treatment was repeated several times, followed by treatment with a HF-$HClO_4$ mixture, $HClO_4$ alone. Finally the residue was dissolved in HCl, filtered through a 0.45 m membrane filter (Gelman DM-450, Metricel). The final solution was made up to a known volume in 0.1 M HCl.

Analysis: Reagents

Basically, for all analyses for Th-230 and Ra-226, the following procedure was used, sometimes with minor adjustments.

Chemicals or solutions needed were:

Lanthanum	1.0 mg La^{+3} ml^{-1} in 0.1 M HNO_3
Barium	1.0 mg Ba^{+2} ml^{-1} in 0.1 M HNO_3
Na_2SO_4	20% solution
HF	6 M
$HClO_4$	2.5 M
$K_2Cr_2O_4$	0.4 M
DTPA	67 gm diethylene triamine pentaacetic acid and 32 gm NaOH pellets in aqueous solution, filtered, made up to 1.0 l and adjusted to pH 10; stored in a polyethylene bottle.
H_2SO_4	9 M

^{133}Ba approximately 500 ds^{-1} ml^{-1}, carrier free in 0.17 HCl, obtained from Amersham.

^{234}Th approximately 500 ds^{-1} ml^{-1}, carrier free, obtained from depleted $UO_2(NO_3)_2$ passed through an anion exchange resin.

Radium Determination

To an aliquot of the digested sample the following carriers and tracers were added:
1.00 ml ^{133}Ba, 1.00 ml ^{224}Th, 1 mg Ba^{+2}, and 1 mg La^{+3}. While stirring, 2 ml 9 M H_2SO_4 per 100 ml solution were added and the solution was left standing at room temperature for 30 minutes. It was filtered through a 0.45 m membrane filter, the filtrate was saved for the Th-230 determination. The filter was transferred to a small beaker, the walls of the filter tower were rinsed with 5 ml DTPA solution which was added to the filter. The solution was heated gently to dissolve the $(Ba,Ra)SO_4$. After this dissolution the filter was removed and rinsed with approx. 15 ml of water.

One ml of 20% Na_2SO_4 solution was added and the pH was lowered to 3.5 with 2.5 M $HClO_4$. The solution was brought to a gentle boil to remove radon. After cooling, the solution was passed through a 0.2 μm membrane filter (Gelman HT-200 Tuffryn). The filter was dried under a heat lamp and measured in the gamma and alpha spectrometers.

Thorium determination

To the filtrate saved for Th-230 analysis, NH_4OH was added to

raise the pH to 8. The solution was left standing for 30 min. at room temperature and if necessary centrifuged prior to filtering through 0.45 μm membrane filter. The filter and precipitate were transferred to a small beaker and 1 ml conc. HCl was added, followed by some water. After dissolution, the filter was removed under rinsing and the volume made up to approx. 50 ml. To this solution 0.3 ml of a 0.4 M $K_2Cr_2O_4$ solution was added to oxidize polonium. The solution was brought to a gentle boil. After cooling, the solution was transferred to a Teflon beaker, and 4 ml 6 M HF was added to precipitate $La(Th)F_3$. After 30 minutes of standing at room temperature the solution was filtered through 0.2 m membrane filter. The filter was dried, mounted with double sided tape and measured in the gamma and alpha spectrometers.

Radioactivity measurements.

The 64 and 93 KeV photopeaks of Th-234 and the 360 KeV photopeak of Ba-133 were used to measure the radiochemical recoveries of Th and Ra respectively. See sketches in Fig. 1. In most cases recoveries of Ba-133 and Th-234 were 90-95%.

The alpha measurements were done in an particle ccccspectrometer with a surface-barrier detector (Ortec BR series, 300 mm^2 of active area). The detectors were calibrated prior to use. Figure 2 showed typical spectra for Th-230 and Ra-226.

Leaching. One gram of the sample was added to 100 ml KCl, 0.1M. The mixture was stirred mechanically at constant r.p.m. At certain time intervals at 10 ml aliquot was withdrawn, filtered through a 0.45 μm membrane filter, collected into a tube

containing 1 ml conc. HCl. The filtrate was analysed for Ra-226 and Th-230 by the above. Times for extracting samples from the leaching solution were: 2, 20, 50, 90, 120 and 180 minutes. Zero time was taken as the sample was added to the stirred solution. In some cases the leaching of samples of tailings with 0.1M HCl was extended to 4.8 days. After analysis, the precipitates obtained containing $^{133}Ba(Ra)SO_4$ and $La(Th)F_3$ were measured in the gamma and alpha spectrometers and the recoveries calculated. The results were tabulated and plotted on graphs.

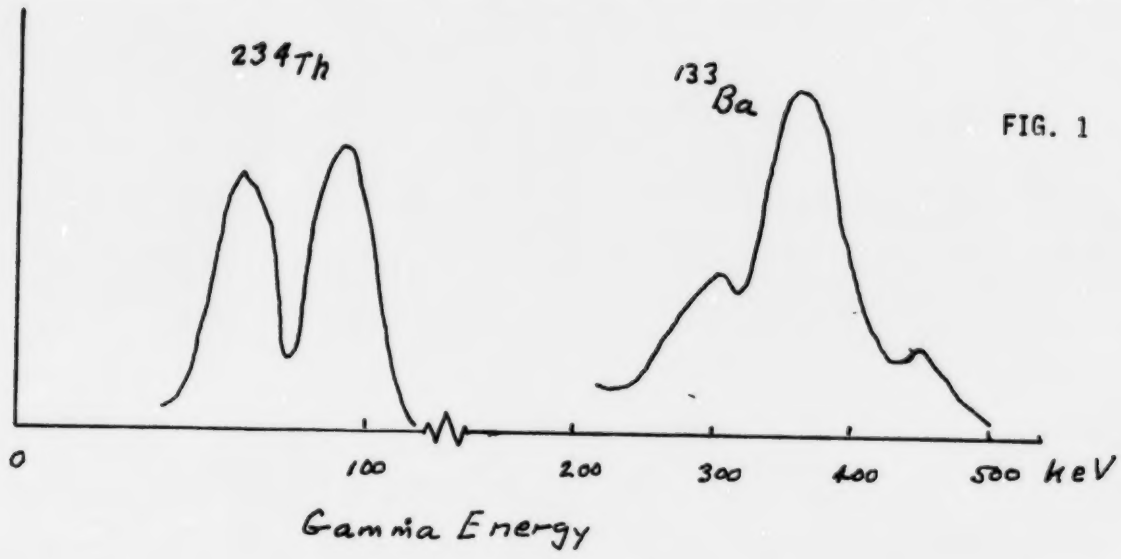
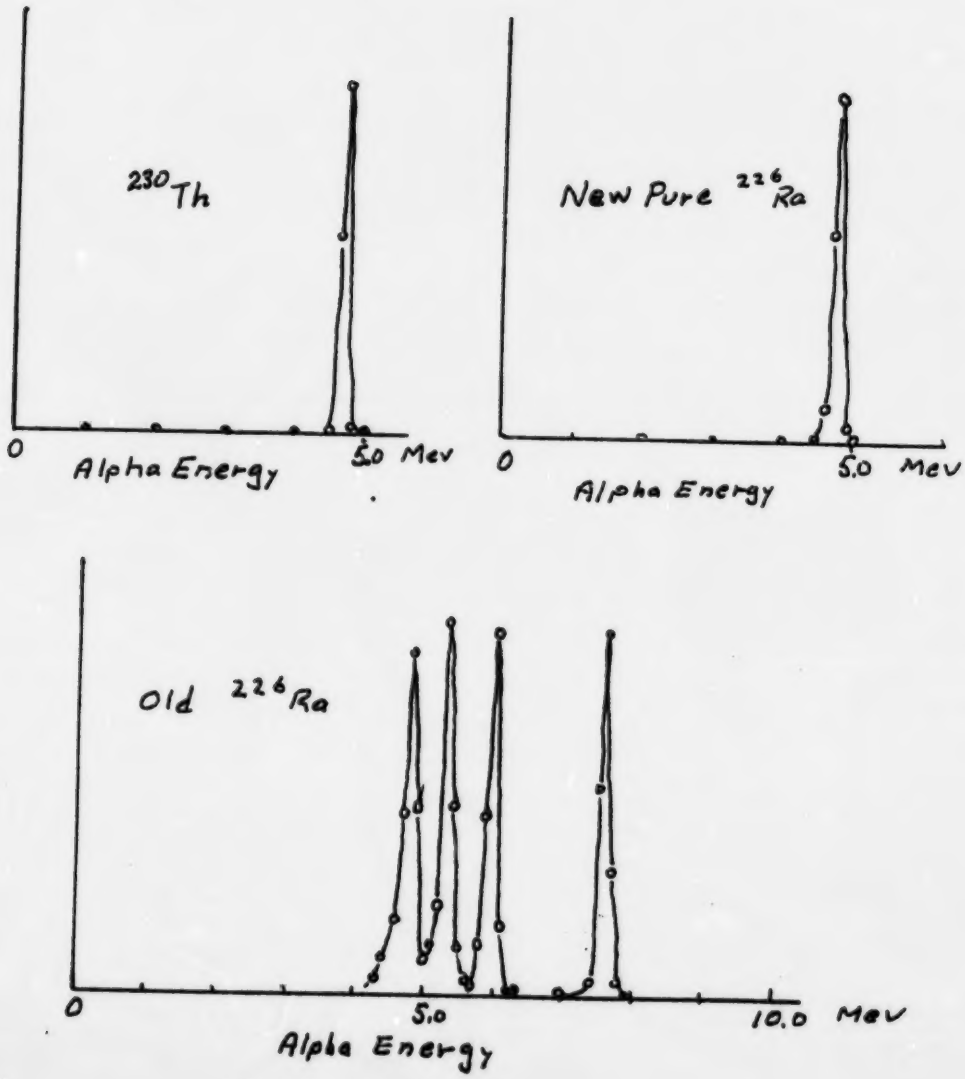

234Th
133Ba
0
100
200
300
400
500 keV
Gamma Energy

FIG. 1

FIG. 2


230Th
0
5.0 Mev
Alpha Energy
New Pure 226Ra
0
5.0 Mev
Alpha Energy
Old 226Ra
0
5.0
10.0 Mev
Alpha Energy

Appendix III

Leaching Experimental Data

The following are representative leaching data from the kinetic leaching study. The statistical uncertainties shown are calculated from the observed counting data and represent the single-value standard deviation.

Sample	Time (min.)	^{226}Ra(pCi)	^{230}Th(pCi)
B-5 comb top	10	3.5+0.5	0.8+0.8
	30	9.1+0.9	0.4+0.4
	60	10.9+0.9	0.8+0.8
	90	10.0+0.9	1.6+1.6
	120	10.8+0.9	0.2+0.2
	180	9.9+0.9	not detected
B-5 comb mid	10	5.8+0.8	n.d
	30	10.8+0.7	0.7+0.2
	60	15.6+1.4	6.0+1.2
	90	22.8+1.6	n.d
	120	13.8+1.3	2.2+0.4
	180	27.3+1.6	0.7+0.3
B-5 comb bot	10	7.4+0.9	n.d
	20	9.8+0.9	0.7+0.2
	60	12.5+0.7	0.9+0.2
	90	18.1+0.9	1.1+0.4
	120	18.1+0.9	2.0+0.4
	180	22.6+1.5	2.3+0.5
B-5 74-12μ microns top	10	38.8+2.1	3.6+0.7
	30	47.9+2.3	4.7+0.9
	60	55.8+2.5	6.4+0.9
	90	63.9+2.6	7.5+0.9
	120	70.4+2.6	7.2+0.8
	180	72.0+2.7	6.5+1.2
B-5 74-12μ microns mid	2	10.9+1.0	1.1+0.3
	20	21.2+1.5	1.9+0.5
	50	22.3+1.5	2.1+0.5
	90	26.4+1.6	2.9+0.5
	120	32.1+1.8	3.2+0.5
	180	36.6+1.9	4.1+0.5
B-5 74-12μ microns bot	2	20.5+1.4	1.8+0.4
	20	23.9+1.5	1.2+0.3
	50	26.0+1.6	3.0+0.6
	90	31.4+1.7	2.6+0.6
	120	38.4+2.0	5.7+0.8
	180	46.2+2.1	3.9+0.6

B-5 -12μmicrons top	2	47.7+2.8	1.9+0.5
	20	53.9+2.7	4.2+0.7
	50	72.4+3.1	6.4+0.8
	90	77.0+2.6	5.2+0.8
	120	75.8+2.6	1.5+0.4
	180	79.9+2.9	2.5+0.5
B-5 -12μmicrons mid	2	39.7+1.9	1.5+0.4
	20	52.5+2.2	1.4+0.4
	50	56.1+2.3	1.9+0.4
	90	52.2+2.2	2.0+0.4
	120	58.9+2.3	2.2+0.5
	180	61.5+2.3	5.0+0.7
B-5 -12μmicrons bot	2	36.9+1.8	2.1+0.4
	20	36.3+1.8	1.0+0.3
	50	38.0+1.9	3.0+0.5
	90	38.8+1.9	2.4+0.5
	120	37.7+1.8	2.4+0.5
	180	43.6+2.0	4.4+0.6
B-1.5 comb top	2	5.6+0.8	1.3+0.3
	20	14.6+1.0	1.4+0.4
	50	23.5+2.0	1.6+0.4
	90	30.3+2.0	1.1+0.3
	120	29.1+2.0	4.7+0.6
	180	26.7+2.0	2.1+0.4
B-1.5 comb mid	2	3.4+0.6	0.9+0.3
	20	13.4+1.0	0.3+0.2
	50	25.5+2.0	1.2+0.4
	90	34.7+2.0	0.9+0.3
	120	51.2+3.0	1.3+0.3
	180	64.6+4.0	8.1+0.8
B-1.5 comb bot	2	2.0+0.5	0.5+0.2
	20	6.5+0.9	0.4+0.2
	50	7.1+0.9	1.1+0.4
	90	14.0+1.0	0.5+0.2
	120	16.5+1.0	0.7+0.2
	180	22.3+2.0	1.2+0.3
H-1.5 comb top	2	10.9+1.1	1.0+0.2
	20	24.8+1.6	1.6+0.3
	50	36.4+2.0	2.0+0.3
	90	40.4+1.9	1.6+0.3
	120	46.7+2.2	2.5+0.4
	180	54.3+2.7	5.9+0.6
H-1.5 comb mid	2	7.0+0.8	0.5+0.2
	20	18.6+1.3	1.1+0.3
	50	27.8+1.7	1.3+0.3
	90	34.8+1.8	0.9+0.3
	120	40.0+1.9	2.2+0.4
	180	40.1+2.0	3.0+0.6

H-1.5 comb bot	2	3.9+0.4	0.3+0.1
	10	6.7+0.5	0.7+0.2
	40	11.9+0.7	0.6+0.2
	80	14.5+1.1	0.8+0.3
	120	16.9+1.2	1.4+0.3
	180	23.0+1.5	1.9+0.4
H-1.5 74-12μ microns top	2	10.6+1.0	0.1+0.1
	20	27.6+1.6	0.5+0.3
	50	39.7+1.8	1.4+0.5
	90	43.6+1.9	1.4+0.5
	120	54.8+2.2	0.3+0.2
	180	61.2+2.2	0.6+0.3
H-1.5 74-12μ microns mid	2	14.6+1.1	0.8+0.3
	20	19.8+1.3	0.7+0.3
	50	31.2+1.7	0.7+0.3
	90	38.0+1.8	0.7+0.4
	120	47.3+2.1	1.5+0.4
	180	68.4+3.0	1.3+0.4
H-1.5 74-12μ microns bot	2	6.7+0.8	0.4+0.2
	20	14.1+1.1	0.5+0.1
	50	16.7+1.3	1.3+0.3
	90	26.8+1.6	2.9+0.4
	120	30.7+1.6	1.3+0.3
	180	34.9+1.8	1.7+0.3
H-1.5 -12μ microns top	2	61.0+2.4	2.3+0.3
	20	64.0+2.4	3.8+0.4
	50	69.8+2.6	2.7+0.4
	90	67.6+2.5	5.5+0.5
	120	67.4+2.1	7.5+0.6
	180	71.6+2.6	3.7+0.4
H-1.5 -12μ microns mid	2	62.3+2.4	3.3+0.5
	20	75.6+2.6	3.8+0.5
	50	83.9+2.5	5.8+0.6
	90	86.2+2.8	8.3+1.0
	120	93.0+2.9	4.2+0.8
	180	92.2+2.9	7.1+0.7
H-1.5 -12μ microns bot	2	17.4+1.3	1.3+0.6
	20	22.3+1.4	-------
	50	25.9+1.5	1.4+0.6
	90	33.6+1.8	0.40.1
	120	33.7+2.1	1.0+0.4
	180	37.4+1.8	2.2+1.1
J-5 comb top	2	4.4+0.7	0.1+0.1
	20	7.0+1.2	2.0+0.4
	50	10.9+1.3	1.5+0.4
	90	15.6+1.4	0.5+0.2
	120	15.5+1.7	2.4+0.4

		180	14.5+2.1	14.1+1.0
J-5	comb mid	2	1.6+0.4	0.2+0.2
		20	1.7+0.5	0.2+0.2
		50	2.3+0.5	0.2+0.1
		90	3.4+0.6	0.3+0.2
		120	4.0+0.6	0.2+0.2
		180	2.0+0.4	0.3+0.2
J-5	comb bot	2	0.9+0.4	0.9+0.2
		22	0.6+0.3	0.4+0.1
		70	1.9+0.6	0.2+0.1
		100	2.0+0.4	0.4+0.1
		150	0.2+0.2	0.9+0.3
		180	1.5+0.4	0.9+0.5
		162	0.8+0.3	0.2+0.1
J-5	74-12μmicrons top	2	19.7+1.4	0.4+0.2
		20	31.9+1.7	0.9+0.3
		50	40.5+2.2	1.2+0.4
		90	45.8+2.0	2.0+0.5
		122	47.1+2.0	0.8+0.3
		180	62.8+2.5	0.5+0.3
J-5	74-12μmicrons mid	: not leached, insufficient material		
J-5	74-12μmicrons bot	: not leached, insufficient material		
J-5	-12μmicrons top	2	49.3+2	4.0+0.4
		20	69.5+5	6.7+1.0
		50	59.8+2	4.1+0.6
		90	55.1+2	6.2+0.7
		120	62.6+3	4.1+0.6
		180	64.5+3	4.4+0.6
J-5	-12μmicrons mid	2	32.5+2.0	1.4+0.3
		20	31.6+1.9	1.3+0.3
		50	36.9+2.1	2.0+0.3
		90	42.4+2.0	1.7+0.3
		120	48.2+2.1	1.4+0.3
		180	49.5+2.2	1.4+0.3
J-5	-12μmicrons bot	: not leached, insufficient material		

Appendix IV

Autoradiographic Procedures

The method of autoradiography is used to locate the sources of highly ionizing radiation. It is of little use for rays, and of some use for rays, especially for the low energy rays from carbon-14, tritium and sulphur-35. Most clearly, it can be used to show α-particle trajectories.

Normally one uses fine-grained black and white photographic film. However, for this work, we preferred a film using a totally different principle - Kodak LR 115A. The advantage is that it is completely insensitive to daylight and also to γ and radiation. Thus it is very convenient for particle track detecting.

This film is composed of a dye-loaded polycarbonate layer 12 microns thick mounted on a thicker polyacetate backing. The alpha particles cause so much damage in the film that the polycarbonate layer is rendered soluble. Thus, a single track can be seen by transmitted light as a bright hole etched in the otherwise red film. These holes have a diameter of only a very few microns, so the mineral grain giving the particle can be identified readily. More refined resolution to identify the area on the grain has been attempted with some success, but suffers from the difficulty of accurately relocating the grains and the autoradiograph with respect to one another. This can be done easily, in many cases, to within 10-20 microns. This is regrettably not usually good enough to permit the high

resolution study of small composite grains. There is, however, no trouble in identifying radioactive grains and fortunately most of those we dealt with in the present report were of single minerals.

Procedure. Grains to be studied are mounted on a glass microscope slide to which a thin layer of paraffin wax has been fixed. (Parafilm serves this purpose.) The grains are gently embedded in the wax using slight heating if necessary. The film is laid on this slide and kept pressed very gently so as to make contact but not scratch the film or move the grain. After an exposure of 100-140 hours, the film is etched in 10% KOH solution at 55°C for 2 1/2 hours. When development is complete the film is washed in water for 30 min. and rinsed in ethanol for 30 sec.

After being dried, the film can be again laid on the slide and is conveniently viewed using both reflected and transmitted light.

Appendix V

Autoradiographic and Photomicrographic Results

a) Autoradiography

The results of the autoradiography experiments have been summarized in Table VI. The individual results and typical autoradiographs are given in the present Appendix. The grains shown in Photos V.1, V.2 and V.3 and described in Tables V.I, V.II and V.III are those separated by simple density experiments, using $CHBr_3$ and CH_2I_2. Thus, their densities will be in the ranges < 2.87, 2.87-3.33 and > 3.33, respectively. The least dense of these fractions is seen in Photo V.1 to be very low in radioactivity, while the densest fraction is seen in Photo V.3 to be distinctly radioactive. This is in keeping with other unpublished results obtained in this laboratory for other tailings samples. In both the dense and the intermediate fractions there are some grains which are not active.

Photos V.4 to V.7 show enlarged autoradiographs of several individual grains. The differences in intensity will be immediately apparent. The anticipated irregular distribution in activity, seen in some other studies (unpublished, Carleton University) is not evident in these photos, owing perhaps to the size of the grains which precludes the required close contact between the surface and the film in order to get good resolution.

It will be noted that the separations undertaken using $CHBr_3$ and CH_2I_2 were very imperfect. This is due to the fact that many of the grains are composites, so that only the overall mean density is of significance.

b) Photomicrography.

The initial purpose of the photomicrographs was to enable us to match up the photographs and the autoradiographs in order to detect and study irregularities in the distribution of radium and thorium on the grain surfaces. The actual autoradiographs failed to show the expected irregularities, either because the distribution is really homogeneous or because the surface roughness destroys our spatial resolution. The photomicrography was not pursued further.

Photo V.1. Autoradiograph of 46 grains, density less than 2.87. (Light fraction from CH_3Br separation)

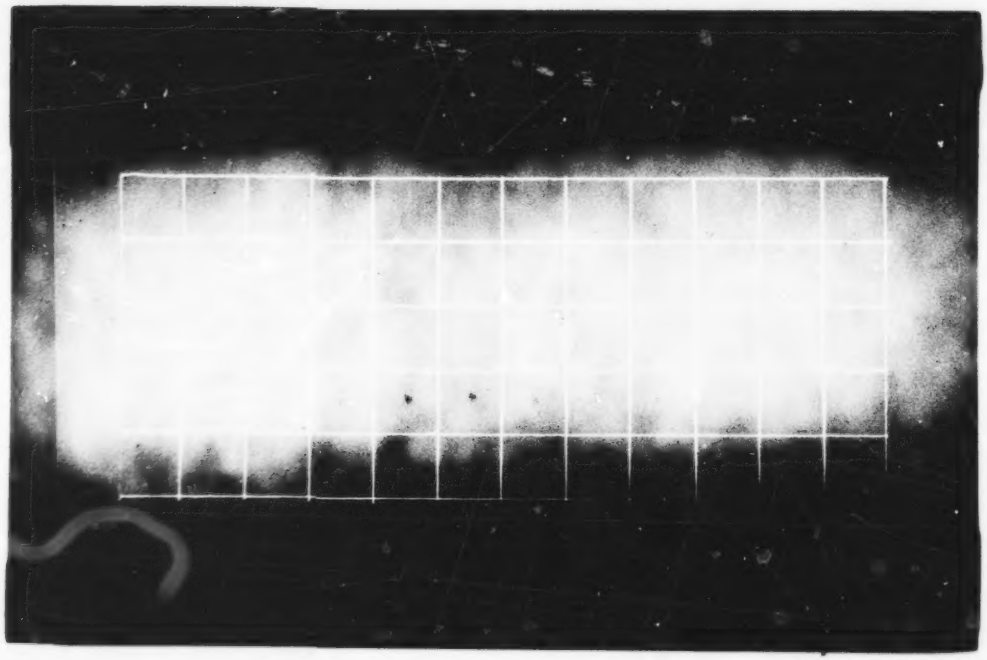


Table V.I. Identification of grains in Photo V.1. Numbering is left to right, in rows numbered top to bottom.

Row 1		All grains are Quartz
Row 2		All grains are Quartz
Row 3		All grains are Quartz
Row 4		1,2 and 3 are Quartz
	4	Quartz and Hematite
	5	Sphalerite ?
	6	K Al Silicate
	7	K Al Silicate
	8	Sphalerite ?
	9	?
	10	Calcite ?

Photo V.2. Autoradiograph of 36 grains, density between 2.87 and 3.33. (Light fraction after CH_2I_2 separation.

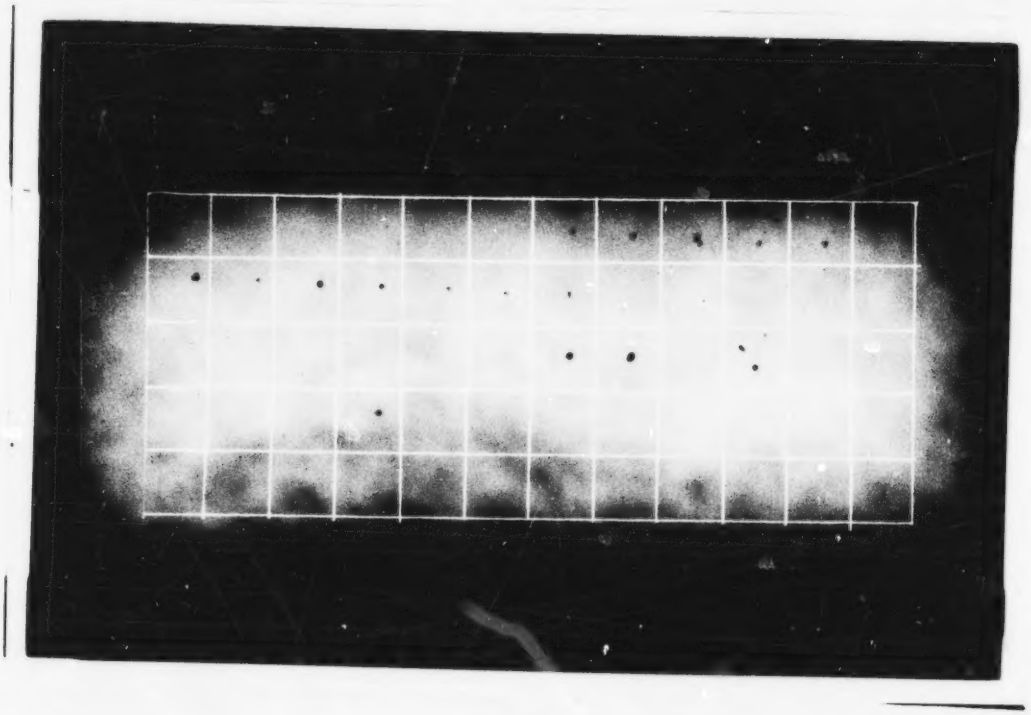


Table V.II. Identification of grains in Photo V.2. Numbering is left to right, in rows numbered top to bottom.

Row 1	1	Annabergite
	2 - 6	K Al Silicate
	7,8	K Al Silicate + UO_2 ?
	9 - 12	Al Silicate
Row 2	1	?
	2 - 7	Hematite
	8 - 12	Amphibole ?
Row 3	1	Amphibole
	2	?
	3 - 5	Quartz
	6	K Al Silicate
	7	Pyrite + UO_2
	8	Amphibole (+ sphalerite ?)
	9	Zircon
	10,12	Sphalerite
	11	?

Photo V.3. Autoradiograph of 36 grains, density greater than 3.33. (Heavy fraction after separation with CH_2I_2)

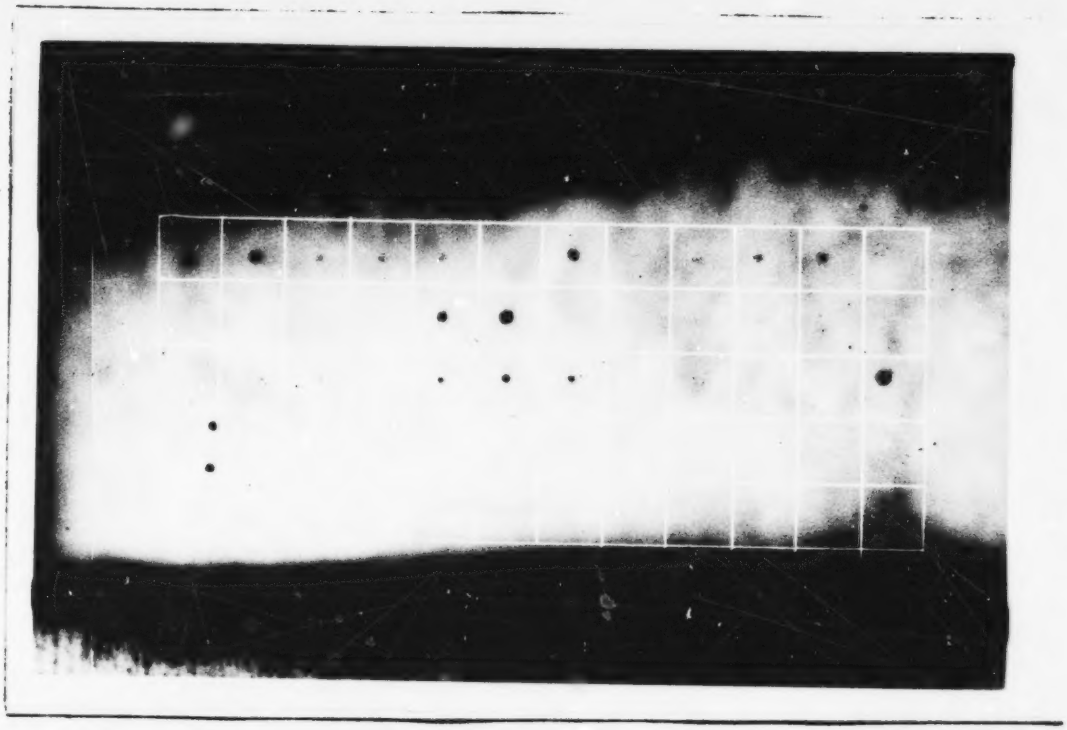


Table V.III. Identification of the grains in Photo V.3. Numbering is left to right, in rows numbered from top to bottom.

Row 1	1 - 5	Hematite
	6 - 8	Annabergite (7,8 + UO_2 ?)
	9	(grain lost)
	10	Hematite
	11	Annabergite (+UO_2 ?)
	12	Biotite
Row 2	1 - 5	Ampphibole (hornblende)
	6	Uraninite
	7 - 12	Chalcopyrite
Row 3	1 - 3	Zircon
	4 - 7	Sphalerite
	8,9	Pyrite (+ UO_2 in 8)
	10	Quartz ?
	11	Rutile
	12	Uraninite

Selected autoradiographs

Photos V.4 to V.7 show enlargements of the autoradiographs of several individual grains. The differences in intensity will be immediately apparent. The anticipated irregular distribution in activity, seen in some other studies (2) was not evident, perhaps because the shapes of the grains made it impossible for the film to be in close contact, thus precluding good spatial resolution.

Photo V.4. Autoradiograph of a grain of uraninite (grain 18 from Photo V.3).

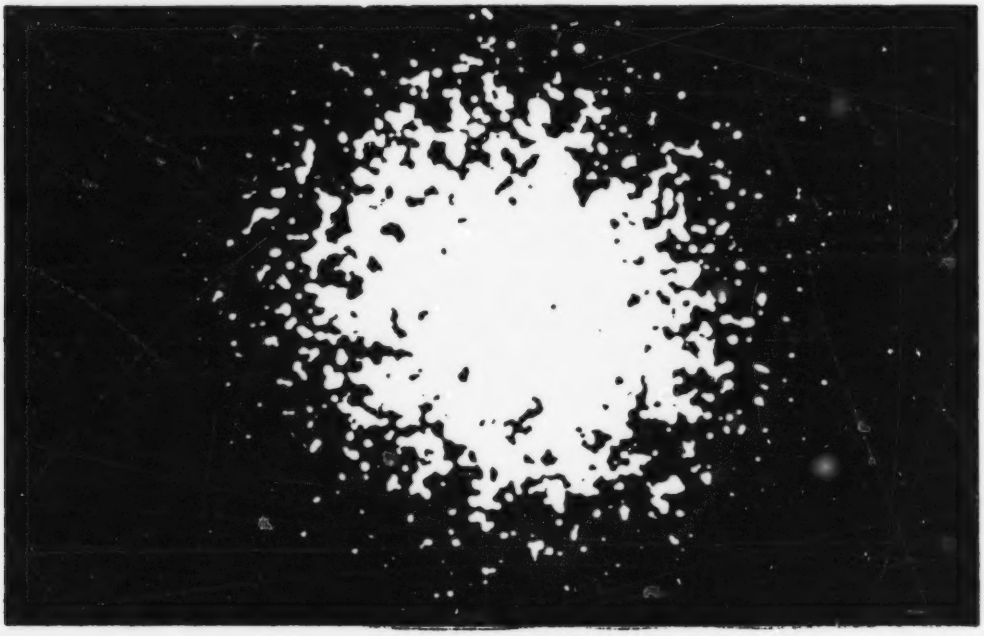


Photo V.5 Autoradiograph of a grain of zircon (Grain 26 from Photo V.3).

Photo V.6 Autoradiograph of a grain of sphalerite (Grain 31 from Photo V.3).

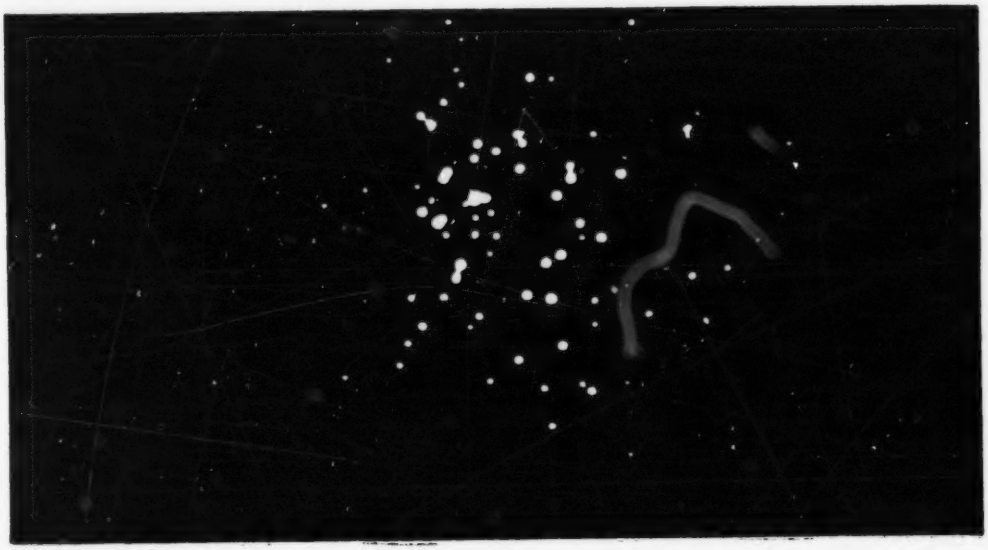


Photo V.7 Autoradiograph of a grain of hematite (Grain 1 from Photo V.3).